Studies on Acetylene and its Derivatives. (XII) Reactions of Aldehydes and Acetylene under Pressure. (2)

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68, 358 (1946); F. P. Price, *ibid.*, 70, 871 (1949)).

There were obtained, on the other hand, dimethyldiethylsilane (III) and methylthylriet silane (IV) as shown in Fig. 2 and Table 1, instead of the disilane derivatives,

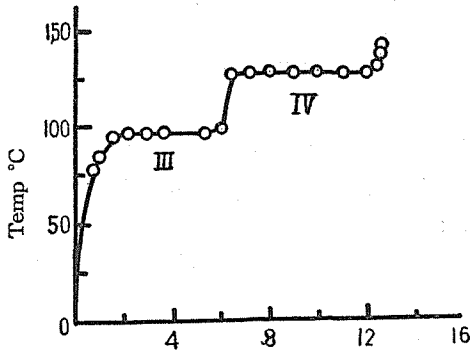

Fig. 2

the fractional distillation of the sulfuric acid-insoluble layer. This apparently unexpected result is probably due to the fission of Si-Si bond in 1, 1, 2-trimethylchlorodisilane, for example, during the Grignad reaction under the conditions employed. Similar phenomena have been already recognized by the several researchers (cf. Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin 1937, p. 268).

From these results, it is known that the compounds containing methyldichlorosilyl and dimethylchlorosilyl radicals exist in this disiloxane fraction.

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18. Studies on Acetylene and its Derivatives. (XII)

Reactions of Aldehydes and Acetylene under Pressure. (2)

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Acetylene was reacted with formaldehyde under pressure using various catalysts, and in order to obtain a superior amount of propargyl alcohol, the selective conditions were investigated.

The following Cu catalysts were used, and the general experimental procedures were similar to that of previous report (read at the 6th annual meeting of Chem. Soc. of Japan).

(A) Single catalysts:

The catalysts were prepared from the following materials.

Cat. 1. cupric oxide (by calcination of cupric carbonate.)

Cat. 2. cupric oxide (by calcination of cupric acetate.)

Cat. 3. cupric carbonate.

Cat. 4. cupric acetate.

Cat. 5. cuprous chloride.

The experimental results were as follows:

1) Water as solvent:

Catalysts 1, 2, 3 and 5 gave similar results, and about 33 % yields of propargyl alcohol was obtained respectively, but catalyst 4 was less active.

2) Methanol as solvent:

Catalysts 1 and 2 showed the same results as above, but catalysts 3 and 4 have no activity.

3) Effect of condition at developing

When the concentration of formaldehyde at developing was increased, the activity of catalyst 1 was improved, but the selectivity of the catalyst did not be varied.

(B) Mixed catalysts.

Catalysts were prepared by the following methods.

Cat. 1. copper-chromite (by calcination of cupric chromate)

Cat. 2. copper-silicate (Silica gel was dipped into the cupric nitrate solution and ignited.)

Cat. 3. copper-silicate (by co-precipitation)

These catalysts showed more desirable activity in both solvents, but the selectivity decreased.

(C) Preparation of propargyl alcohol and butynediol

In a shaking stainless steel autoclave of 740 c.c. capacity, a mixture of 60g. paraformaldehyde, 150g. methanol and 20g. (A) catalyst 1. was put in. After acetylene was compressed to 19 atm. at 20°, the autoclave was heated to 110~115°. The pressure rosed about to 40 atm. and fell to 20 atm. during seven hours.

Methanol was distilled off and the residue was distilled under reduced pressure (20~30 mm. Hg) on the steam bath. The distillate was dried with $CuSO_4$ and fractionated. Propargyl alcohol boiling at 112~113° was obtained in 30g. yield. (23 % of the theoretical amount)

The residue, from which propargyl alcohol was distilled off, was supplied to diminished pressue distillation. The yield of butynediol boiling at 115°/4mm., melting at 58° (recrystallized from acetone) was 47g. (54 % of the theoretical amount).